

# Telomer Research Program

**Annual Report of Activities for TRP Grant to University of Toronto;  
Scott Mabury, PI**

**Project years: 1 September, 2001 to 1 September, 2002.**

**Students/PostDocs currently active on the FTOH project:**

Postdocs: Dr. David Ellis, Dr. Jon Martin, Dr. Stella Melo,

Grad students: Naomi Stock, Ella Ye,

Undergrad Students: Kerry Pratt, Fiona Lau, Ryan Sullivan, and Lisa Deeleebeck.

**Note:** TRP funds support the research of Dr. David Ellis while other funds support the rest of the team.

**Academic Co-Investigators:** Derek Muir (NWRI), Keith Solomon and Paul Sibley (UofGuelph), Kim Strong (Toronto-Physics), Tim Burrow (Toronto; Chemistry; NMR Facility), Ying Lei (Toronto; Chemistry; ANALEST).

**Project Coordination:** During the initial year of the project the UofT research team hosted TRP visits in Fall, 2001 (Libre, Hoke, Buck, Kaiser) for a general research progress, a priorities setting exercise, Winter, 2002 (Kaiser and Gearhart) for familiarization with our analytical techniques for FTOH air sampling/analyses and a late spring 2002 'update' meeting with Libre, Hoke, and Buck. Further there were at least 2 conference calls concerning air sampling and vapour pressure measurements that transpired during this period. A number of visits prior to Sept, 2001 also occurred both in Toronto and Guelph to explore research interests and analytical techniques.

**Status of NSERC.Strategic Matching Funds:** A proposal was submitted in mid-April to NSERC to pursue additional funds for our FTOH work. This proposal has Mabury as PI and Muir, Sibley, and Solomon as Co-Investigators. Notification of success in this grant cycle will likely be in November.

**Specific Objectives for TRP funds for Year 1 (from the research agreement appendix):** *Based on the October 26, 2001 meeting that included the Mabury (Toronto), Muir (NWRI) and Sibley (Guelph) and Hoke, Buck, and Kaiser (Dupont) and Libre (Atofina) the specific work to be continued and expanded for the **TRP** funded portion of this project is to focus in year 1 on three specific areas and include the following: 1) **analytical methodologies**; 2) **environmental monitoring** and 3) **environmental fate determination**. Analytical methods will directly focus on further optimizing our sampling and GC-based analysis techniques of fluoro-telomer alcohols*

*primarily in air samples and developing the basic methods utilizing lc/ms/ms to determine our hypothesized degradation products which are the telomer-acids. Environmental monitoring will comprise air sampling at Toronto in an ongoing campaign and an intensive air sampling at selected locations across North America. Initial samples for telomer degradation products will also be run focusing on atmospheric particles and municipal outfalls. Our main objectives in the environmental fate area are to determine degradation pathways and kinetic rates for atmospheric pathways and further refine our physical property measurements.*

Good progress has been made in each of these areas and is reported below. A large air sampling study (FAMAS) conducted last November and an arctic sampling expedition this July, smog chamber experiments, initial experiments investigating biodegradation pathways, and further experiments focusing on physical property measurements of FTOHs and polyfluorinated alkyl chains, have taken up the bulk of effort during our inaugural year of TRP funding.

## **Environmental Monitoring**

### **1. Fluorinated Telomer Alcohols in the North American Atmosphere (Stock, Martin, Lau)**

The presence of fluorinated telomer alcohols and other fluorinated compounds in the North American atmosphere was investigated using high-volume air samplers. In November 2001, samples were collected in six cities throughout North America, which were chosen as remote locations or for nearby presence of industrial sources (Winnipeg MB, Long Point ON, Reno NV, Cleves OH, Toronto ON, and Griffin GA). This study was given the acronym "FAMAS" for **fluoroalcohol monitoring in air samples**. Both gaseous and particulate-bound fluoroorganics were collected on media consisting of XAD-2, polyurethane foam and quartz fiber filters. All samples were approximately 1000 m<sup>3</sup>. Due to the potential for contamination all sample preparations and subsequent extractions were conducted in Class 100 clean room conditions. Briefly, these samples were extracted in large custom, glass columns by soaking in methanol and five aliquots of ethyl acetate. The aliquots were combined and an internal standard was added. The samples were rotovapped to ~ 5 mL, filtered using a nylon 0.2 µm filter and subsequently reduced to ~200 µL under pure nitrogen. Blank extraction samples were also run. Samples were separated using gas chromatography (either 30 or 60 m DB-35 column with 5 micron film) and detected using chemical ionization mass spectrometry (GC/CI-MS) (quadrupole instrument). Several fluorinated compounds - including fluorotelomer alcohols and perfluoro-sulfonamides - were detected at pg/m<sup>3</sup> concentrations in all locations (Table 1). Low concentrations of fluoroorganics were consistently detected in field blanks; however, this did not prevent confirmation or quantification of environmental concentrations. As the sample extraction

method lacked an adequate clean-up step, chromatography difficulties were unavoidable. This proved especially true for the 10:2 FTOH where adequate chromatography was not achieved and thus no quantitative data are reported. Currently, a clean-up step is under development and samples will be cleaned-up and re-analyzed. In addition, the samples will also be analyzed via gas chromatography coupled with tandem mass spectrometry (GC/ MS/MS) (ion-trap instrumentation). We believe this will provide a more robust analytical technique with the added value of MS/MS spectra for enhanced identification. **Table 1.** Concentration of fluorotelomer alcohols (FTOHs) and perfluorooctane sulfonamidoethanols (FOSEs) in North American air samples.

<b>SAMPLE LOCATION</b>	<b>6:2 FTOH (<math>\mu\text{g}/\text{m}^3</math>)</b>	<b>8:2 FTOH (<math>\mu\text{g}/\text{m}^3</math>)</b>	<b>NEtFOSE (<math>\mu\text{g}/\text{m}^3</math>)</b>	<b>NMeFOSE (<math>\mu\text{g}/\text{m}^3</math>)</b>
Cleves, OH	$72 \pm 48$	$79 \pm 35$	$11 \pm 10$	$18 \pm 5$
Griffin, GA	*	$127 \pm 71$	$40 \pm 7$	$371 \pm 309$
Long Point, ON	$16 \pm 5$	$21 \pm 12$	$6 \pm 4$	$10 \pm 4$
Reno, NV	$51 \pm 9$	$50 \pm 7$	$506 \pm 217$	$152 \pm 48$
Toronto, ON	$62 \pm 28$	$25 \pm 22$	$38 \pm 46$	$31 \pm 4$
Winnipeg, MB	$26 \pm 24$	$18 \pm 3$	$27 \pm 6$	$64 \pm 18$

- chromatography difficulties

## **2. Fluorinated Telomer Alcohols in the Lake Ontario Ecosystem (Stock)**

In June 2002, Naomi Stock (PhD student) participated in a 5-day research cruise, aboard the *CGCS Limnos*, of Lake Ontario. At each of three stations, water, sediment, zooplankton and phytoplankton samples were collected. Air samples, using high volume air samplers and polyurethane foam/XAD-2 sampling media (as previously described), were also collected for the duration of the cruise. Currently, methods are being developed to analyze these samples for a suite of fluorinated compounds including the fluorinated telomer alcohols and possible degradation products. Briefly, air samples will be extracted and analyzed via gas chromatography coupled with mass spectrometry as previously described. Water samples will be concentrated onto XAD-7, extracted using a method similar to that employed for air samples and analyzed via liquid chromatography coupled with tandem mass spectrometry. Sediment and biota samples will be extracted using an ion-pairing agent and also analyzed via liquid chromatography coupled with tandem mass spectrometry.

## **3. FTOHs in the Arctic? (Martin, Stock)**

Using additional funding provided by the Northern Contaminants Program (NCP), Drs. Martin and Mabury traveled to Kuujjuarapik (Quebec) between the dates of July 11<sup>th</sup> and 17<sup>th</sup>, 2002, for collection of multiple environmental samples. Kuujjuarapik is located at the mouth of the Great Whale river on the eastern shore of Hudson Bay, just north of James Bay. This location is subarctic, and was chosen primarily because it is an

intermediate distance between the high population density of the Great Lakes region and the Canadian Arctic. The University of Laval also has a research center at this location (Centre D'Etudes Nordiques) which provided us with boats and other necessary sampling equipment.

To test the hypothesis that telomer alcohols (and 3M sulfonamidoethanols) can be transported to remote regions, an air sampler was installed in Kuujjuarapik to collect air samples by the same method as Martin et al.. To date we have collected only two samples, along with a field blank, but the sampler is still installed and we hope to take continuous samples if any telomer alcohols are detected in the existing samples that have yet to be extracted and analyzed. It is expected that air sample data will complement the smog chamber work, allowing for a better understanding of the long-range transport potential for telomer alcohols.

Water and biota samples were also collected for the purposes of our NCP project (Table 2) (i.e. analysis of perfluorinated acids) but will also be analyzed for fluorinated neutrals (including telomer alcohols) when appropriate methods have been developed for extraction and analysis of tissues. Water samples (40 L) were collected in Hudson Bay and in the Great Whale River by pumping water through XAD columns in the field. Sampled biota included phytoplankton, zooplankton, and fish. Even if air samples reveal no traces of fluorinated neutrals (i.e. due to detection limits), biota may reveal traces because of the predictably high bioaccumulation potential for the longer chained telomer alcohols.

Table 2. Biotic and abiotic samples collected in Kuujjuarapik, Quebec.

Sample	Details	Status
Kuujjuarapik Air	2 samples, 1 blank	Cold Storage
Hudson Bay Water	3 samples (40 L each)	Cold storage
Great Whale River Water	1 sample (40 L), 1 blank	Cold storage
Fish Livers	Pike (1), Whitefish (2), Suckers (3), sculpin (2), Trout (1).	Frozen
Hudson Bay Phytoplankton	500 grams	frozen
Fresh Water Zooplankton	3 locations- Mixed Copepods, chironomids, cladocera, diptera, rotifera, calanoida.	frozen

## Physical Properties

**4. Vapour Pressure by the GC method (Le).** The GC retention time method by Bidleman (1981) was chosen, because it allows the relatively rapid determination

of the temperature dependent vapor pressure of a large number of compounds. Small quantities of the substances are sufficient, and a very high purity is not required. Based on a comprehensive review Delle Site (1997) concluded that this method “can be recommended as one of the most suitable [methods] for the determination of the vapor pressure of low volatility compounds.” Another recent study concluded that capillary GC is capable of providing vapor pressure data for non-polar and slightly polar compounds with relative errors that “are either comparable with or lower than those resulting from more cumbersome direct experimental techniques” (Svoboda and Koutek, 2002). The method’s success and reliability however is dependent on the availability of high quality vapor pressure data for some related compounds to serve as standard reference and calibration compounds.

Isothermal gas chromatographic retention times at six temperatures within the range 30 to 80 °C were determined. Super-cooled liquid vapor pressures  $P_L$  were obtained from these retention times following the procedure described by Bidleman (1981) and Hinckley et al. (1990). Specifically, for each analyte a vapor pressure  $P_{GC}$  at 25 °C was calculated using:

$$\ln (P_{GC}/Pa) = (\Delta_{VAP}H / \Delta_{VAP}H_{ref}) \cdot \ln (P_{Lref}/Pa) + C \quad (1)$$

where  $P_{Lref}$  and  $\Delta_{VAP}H_{ref}$  refer to the well-established liquid phase vapor pressure at 25 °C and the enthalpy of vaporization of a standard reference compound. The enthalpies of vaporization are assumed to be constant over the temperature range from 25 °C to the temperatures of the GC retention time measurements. The enthalpy ratio  $\Delta_{VAP}H / \Delta_{VAP}H_{ref}$  and the constant  $C$  in eq (1) were obtained by linearly regressing the logarithm of the ratios of the measured isothermal GC retention times  $t_R/t_{Rref}$  at each temperature against the logarithm of the vapor pressure of the reference compound at that temperature using the relation (Bidleman, 1981),

$$\ln (t_R/t_{Rref}) = [1-(\Delta_{VAP}H / \Delta_{VAP}H_{ref})] \ln (P_{Lref}/Pa) - C \quad (2)$$

Eq 2 assumes that the infinite dilution activity coefficients in the stationary phase are the same for both the analyte and the reference compound (Hinckley et al., 1991). As this is an approximation,  $P_{GC}$  is not always identical to the vapor pressure of the (super-cooled) liquid  $P_L$ , and a calibration of the method with closely related compounds is advisable (Bidleman, 1981, Hinckley et al., 1990). In the current study, hexachlorobenzene served as the standard reference compound. For the calibration we employed the following compounds with well established vapor pressure at 25 °C: 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,2,3 trichlorobenzene, 1,2,4-trichlorobenzene, 1,3,5-trichlorobenzene, 1,2,3,4 tetrachlorobenzene, 1,2,3,5-tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, Pentafluorotoluene, Pentafluorophenol,

TCTFB, Octafluorophthalene, decafluorobiphenyl,  $\alpha$ -HCH,  $\gamma$ -HCH,  $\delta$ -HCH, Aldrin, Heptachlor, Dieldrin, *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT.

**Table 3.** Vapour pressure values for FTOHs obtained using the GC retention time method.

	<b>Log PGC</b>	<b>PGC</b>	<b>log PL</b>	<b>PL</b>	<b>PL</b>	<b>PL</b>
<b>25°C</b>	mean	mean	mean	mean	stdev	RSD
4:2 FTOH	2.401	252	3.18	1514.4	321.4	21%
6:2 FTOH	2.161	145.2	2.90	801.7	149.0	19%
8:2 FTOH	1.662	45.90	2.33	212	34	16%
10:2 FTOH	1.123	13.27	1.70	50	7	13%

##### 5) Measurement of Vapor Pressure by Boiling Point Method (Deeleebeck, Ellis)

The vapor pressure (Vp) of the liquids 4:2, 6:2, 8:2 and 10:2 telomer alcohols were measured using the boiling point method. This method involved a 25 mL round bottom flask connected to a miniature thermometry adapter and condenser; 15 mL of the analyte was added to the round bottom flask. In the case of fluorinated materials, they were first de-gased by a procedure which involved cooling the mother liquor to -198°C

Table 4. Test Chemicals, Vp (Pa)

<b>Compound</b>	<b>Experimental</b>	<b>Literature</b>	<b>difference</b>
<b>Cyclohexane</b>	15720 +/- 3	13370	18%
<b>Toluene</b>	6400 +/- 200	4910	30%
<b>m-Xylene</b>	2900 +/- 100	2250	29%

(liquid N<sub>2</sub>) followed by warming to room temperature while a vacuum was maintained at ~ 15 mmHg. Following this the pressure of the system was reduced appropriately and allowed to equilibrate. The analyte was then brought to its boiling point and the temperature and pressure recorded. This procedure was repeated for decreasing values of pressure, which were achieved by removing the air from the apparatus with a vacuum pump. To determine the vapor pressure at 25 degrees centigrade, the natural log (ln) of pressure in Pascal's was plotted against the temperature in Kelvin. The best linear fit to

the data points was used to extrapolate the boiling point of the chemical at 298 K, the vapor pressure at room temperature. The method was first calibrated using cyclohexane, *m*-xylene, and toluene and the vapor pressures measured were compared with typical literature values ( $n = 3$ , Table 4). The same method was then applied to the telomer alcohols, the results are presented in Table 5 ( $n=3$ ). The telomer Vp's were compared with literature values for the corresponding hydrogenated versions, i.e. fluorine replaced with hydrogen. The increase in Vp associated with the incorporation of fluorine is seen clearly in Figure 1. The rate of decrease in Vp for the telomers as a function of increase in mass is much slower than would normally be expected when compared with their hydrocarbon counterparts, resulting in the vapor pressure of the 8:2 being similar to that of octanol (Figure 2).

Table 5. Telomers, Vp (Pa)

Compound	Run 1	Run 2	Run 3	Average	Std. Dev.
4:2	998	1022	956	990	30
6:2	784	663	692	710	60
8:2	247.7	247.7	272.1	250	20
10:2	138.00	138.2	156.8	140	10

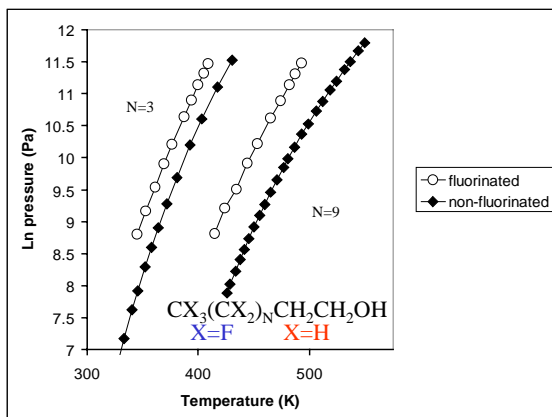


Figure 1. Change in vapor as a function of temperature

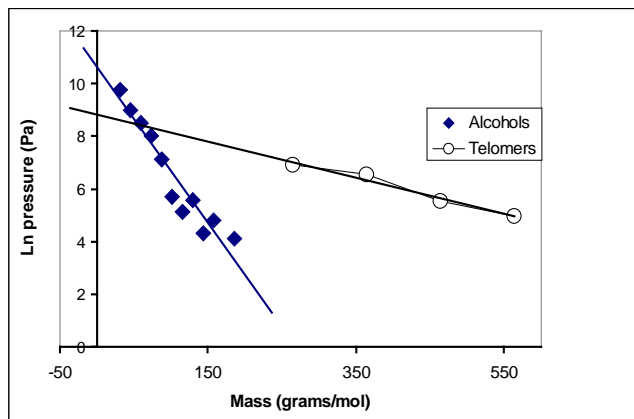


Figure 2. Change in Vapor Pressure a function of mass.

## 6. Measurement of chain rigidity of perfluorinated fluorinated compounds by NMR (Pratt, Ellis, & Burrow)

The physical properties, such as vapor pressure or  $K_{ow}$ , of fluorinated molecules will be determined, to some degree, by the internal molecular geometry of the molecule.

Interaction of the fluorine nuclei result in  $^{19}\text{F}$  NMR coupling constants. The magnitude of these coupling constants is a function of the torsional angle between adjacent C – F moieties. The amount of energy required to allow free rotation between two adjacent C – F units is proportional to the “stiffness” of the alkyl chain, which in turn is related to the Vp of the molecule. 1D  $^{19}\text{F}$  NMR is inadequate in the determination of long range coupling constant in perfluoroalkyl chains due to spectral overlap. We have developed a 2D  $J$ -resolved experiment that facilitates these measurements for which an example is shown for perfluorobutanoic acid in Figures 3a & b.

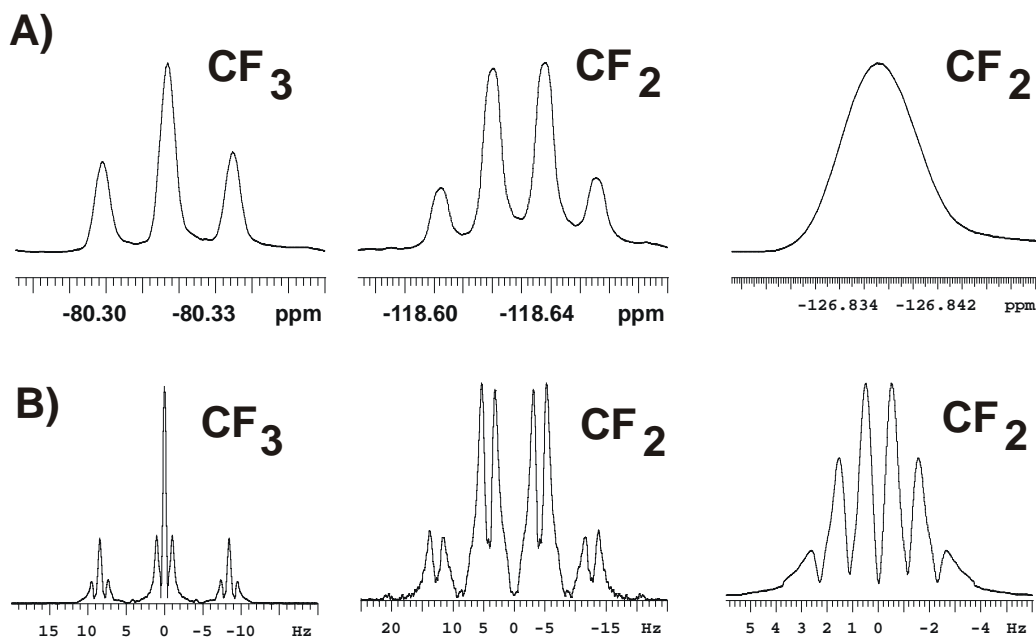


Figure 3. A) 1D  $^{19}\text{F}$  NMR for perfluorobutanoic acid with spectral overlap and B) 2D  $J$ -resolved NMR now showing coupling constants for all fluorine atoms.

This method allowed for the assignment of all fluorine coupling constants and furthermore indicated that at room temperature perfluorobutanoic and longer chain acids have a rigid back bone structure between the  $\text{CF}_2$  units, with free rotation allowed around the  $\text{CF}_3$  –  $\text{CF}_2$  bond. This molecular rigidity facilitates interpretation of the underlying origins of the high Vp of polyfluorinated materials seen in our vapour pressure measurements.

The enthalpy of free rotation of the carbon backbone of the acid was established using variable temperature NMR. A comparison between the effect of chain length and the amount of energy required for free rotation was made. Figure 4 shows a temperature dependent plot of the 1D NMR for the  $\text{CF}_3$  group and two identical  $\text{CF}_2$  groups for the perfluoro -octanoic and -butanoic acids. The coalescence point for butanoic acid is seen at 60°C while it is 90°C for the octanoic acid. This indicates that a perfluoro chain becomes energetically more rigid as a function of chain length and is thus less easily distorted. The results assist in explaining the minimal change in vapor pressure as chain length increases.



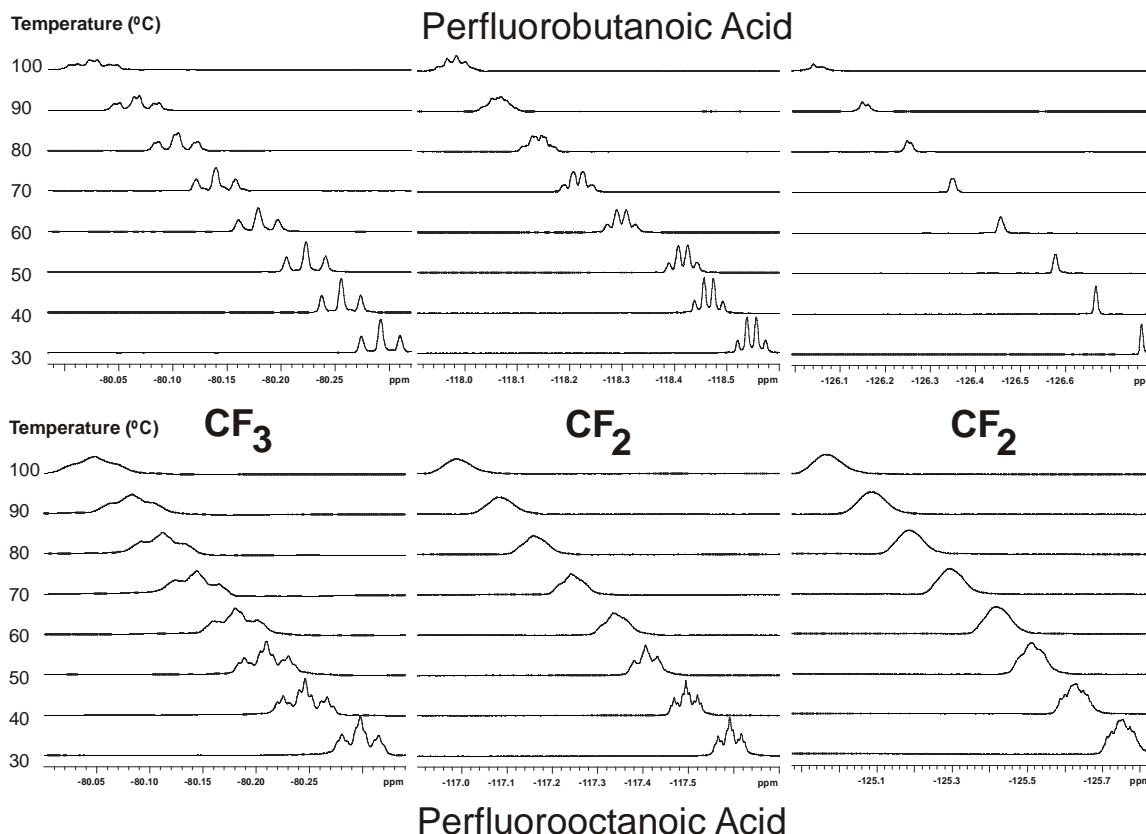


Figure 4. Temperature dependent  $^{19}\text{F}$  NMR for perfluorobutanoic and octanoic acids

## 7. Global Warming Potentials of Fluorinated Telomer Alcohols (Stock & Melo)

In collaboration with Prof. Kim Strong (Department of Physics, University of Toronto), Dr. Stella Melo (Postdoctoral Fellow) and David Barclay (undergraduate student), our research group is in the process of measuring the absorption cross sections of the 4:2, 6:2, 8:2 and 10:2 FTOHs. These cross section measurements are obtained in the infrared atmospheric window at a range of temperatures and pressures. Once the absorption cross section measurements are complete we can calculate the radiative forcing for this polyfluorinated materials, and ultimately calculate a global warming potential of each fluorinated telomer alcohol once we have the accurate lifetime data from our smog chamber studies (see below). It is not expected that the FTOHs will have high GWP but they may have extremely high radiative forcing values due to the large number of C-F bonds (e.g. 21 in 10:2 FTOH).

## Analytical Methodologies

### 8) Synthesis of isotopically labeled internal standards (Ellis & Sullivan)

The synthesis of an isotopically labeled 6:2 aldehyde (M + 2 molecular ion) has been conducted and will be converted to the 6:2 alcohol (M +3) according the scheme outlined in Figure 5 for use as internal standards in the analysis of these and related chemicals.

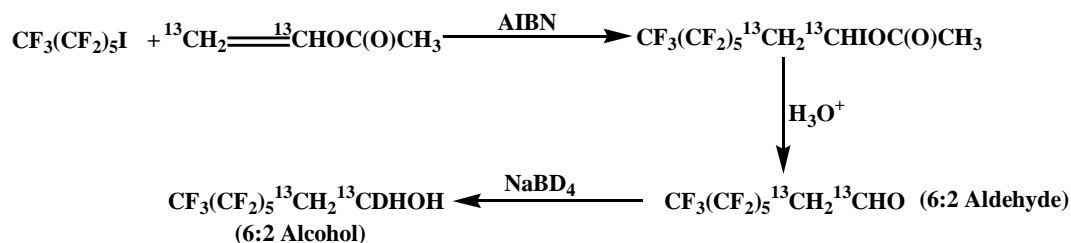


Figure 5. Synthesis of labeled 6:2 aldehyde and alcohols.

### 9) Mass Spectroscopic Studies of Telomer Alcohols and Products (Ellis)

A systematic mass spectrometry study of the telomer alcohols along with their oxidized products, saturated and  $\alpha$ ,  $\beta$ -unsaturated fluoroacids, was conducted using negative and positive chemical ionization (NCI and PCI). The compounds investigated are shown in Table 6.

Table 6. Chemical I.D. and acronymns for the telomer based chemicals used in the MS study.

Telomer Alcohols	Telomer Acids	Telomer $\alpha\beta$ -Unsaturated Acids
$\text{CF}_3(\text{CF}_2)_n\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$	$\text{CF}_3(\text{CF}_2)_n\text{CF}_2\text{CH}_2\text{C(O)OH}$	$\text{CF}_3(\text{CF}_2)_n\text{CFCHC(O)OH}$
n = 2 (4:2)*	n = 2 (4:2A)	n = 2 (4:2UA)
n = 4 (6:2)	n = 4 (6:2A)	n = 4 (6:2UA)
n = 6 (8:2)	n = 6 (8:2A)	n = 6 (8:2UA)
n = 8 (10:2)	n = 8 (10:2A)	n = 8 (10:2UA)

\* Acronymns are given for each in parenthesis.

In the case of the fluoroalcohols, NCI resulted in the production of more elaborate spectra than the other classes. Moreover, it showed the interesting production of  $\text{HF}_2^-$  and the complexation of this species with the parent molecule (Figure 6).

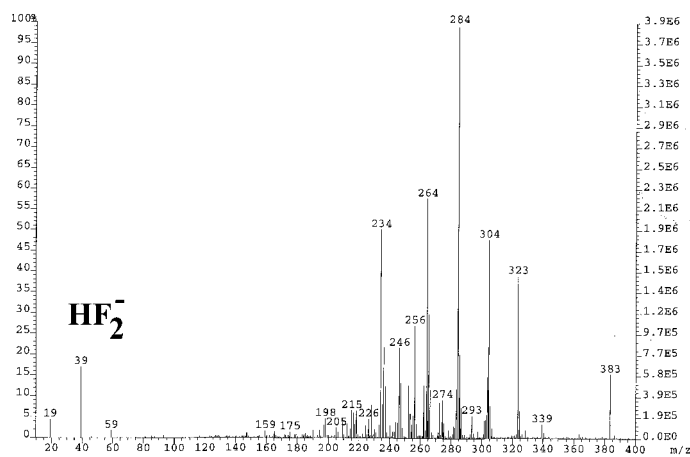


Figure 6. NCI mass spectrum for the 6:2 alcohol showing the production of  $\text{HF}_2^-$

Alteration of the functional group attached to fluoroalkyl moiety had a large impact upon the fragmentation channels, which were identified (see, for example, Figures 12a and b) and also on the magnitude of fragment produced.

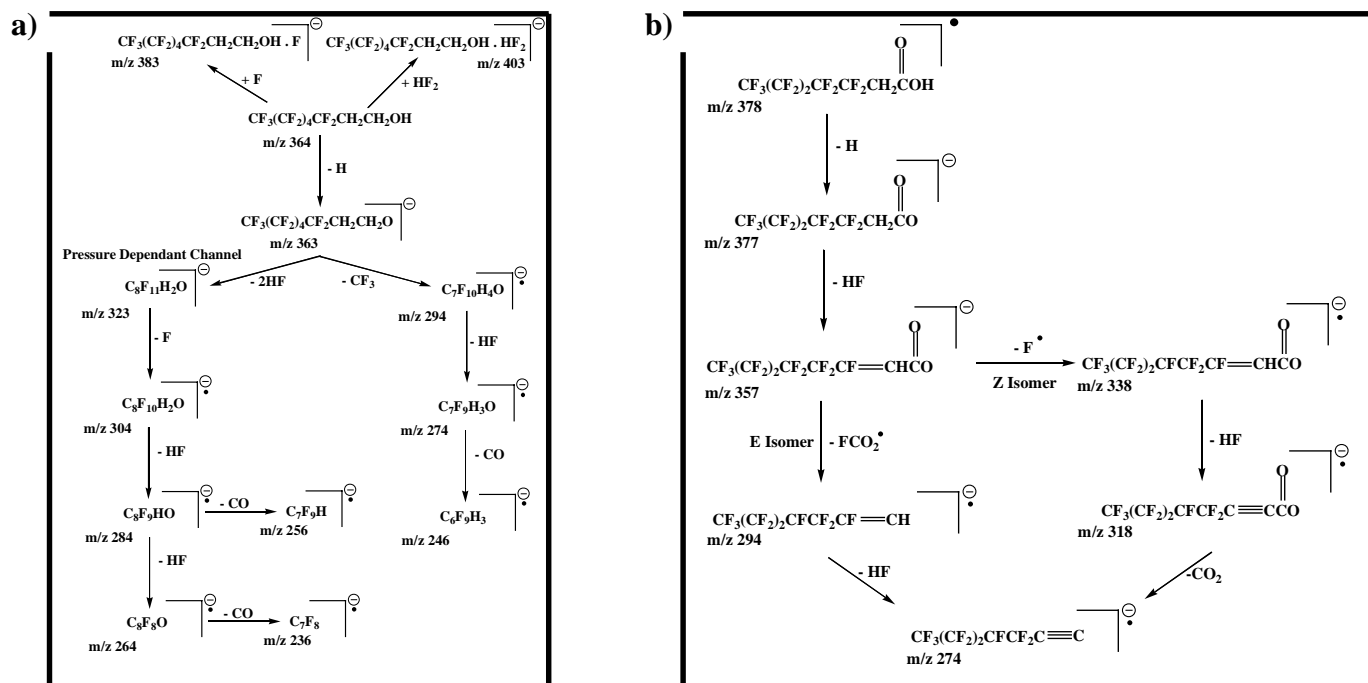


Figure 7. a) Hypothesized fragmentation pattern for the 6:2 telomer alcohol in NCI mode and, b) fragmentation pattern for the 6:2 telomer acid.

Although the exact structure of these intermediates requires further investigation, other researchers, in the case of hydrofluorocarbons, have invoked a six membered back bonding transition state between the hydrocarbon portion of the chain and the fluorocarbon portion to support the sequential loss of HF in similar systems (Napoli *et. al.*). Previous x-ray crystallographic studies suggest that the perfluoro- portion of the molecular chain adopts a ridged zigzag geometry with the end hydrocarbon segment of the chain folding back on top of that fluorinated portion (Wang and Ober, Erkoc and Erkoc). It has also been shown that there is evidence for the cleavage of the  $\text{CF}_2 - \text{CH}_2$  bond within the molecule suggesting there is unusually high stability of this bond which could be explained by a H---F bridging interaction.

Such intramolecular interaction in the case of telomer alcohols in the liquid phase is supported by the studies conducted by Von Werner and Wrackmeyer. They showed that fluorination in the  $\beta$  position to a  $\text{CH}_2\text{OH}$  group had a marked effect on the  $^{13}\text{C}$  NMR chemical shift while having little effect upon the  $\alpha$   $\text{CH}_2$ , an effect which has been assigned to the hyperconjugative interaction of the lone pair of electrons of the fluorine at that carbon. In later studies Von Werner and Wrackmeyer also employed  $^{17}\text{O}$  NMR and showed that electron density at the oxygen is increased as observed through the oxygen shielding effect. This strongly suggests that the terminal ethanolic group is closely associated with the fluorocarbon portion of the molecule. We believe it is this association, and with it changes in electron density distributions, that lead to the favoured complexations of  $\text{F}^-$  and  $\text{HF}_2^-$ . Furthermore, this association would not occur in the case of  $\text{CF}_3\text{CH}_2\text{CH}_2\text{OH}$  and thus this molecule would exhibit differences in its physical and reactive properties relative to the Telomer alcohols.

Detailed analysis and comparisons of the mass spectral data obtained collectively from all analytes allowed certain conclusions to be drawn concerning their thermodynamic physical properties and from this hypotheses can be made toward environmental fate. For example, the unique geometries associated with the compounds and the resultant effect this imparts upon the physical properties may lead to novel and interesting chemistries in the atmospheric gas phase. For example, these results suggest that the telomer alcohols may have a close association, an association that one would not expect for alcohols, with tropospheric charged species and/or polar species as evidenced from their universal association with  $\text{F}^-$  and  $\text{HF}_2^-$ . Complexation with gas phase species such as sulphate, or even with non-charged polar molecules such as water vapor, may effect their dissemination. Atmospheric lifetimes, for example reaction rates with tropospheric cleansing reagents such as hydroxy radicals may also be effected by such complexations, allowing longer-range transport.

It would appear from the fragmentation that occurs that the lowest energy pathway for the degradation of the alcohols, either biotically or abiotically, would result in the production of stable polyfluorometabolites, which in turn might be expected to be environmentally persistent. From these results, it can be postulated that the electron density distribution associated with such unique structural geometries will impact physical properties such as vapor pressures, (e.g. vapor pressures will be greater than expected from linear predictions based upon the molecules size and functional groups)

which is indeed experimentally observed to be the case. The unique differences in geometry of these molecules is also expected to influence physical properties of the molecules such as  $K_{ow}$  and hence bioaccumulation. This postulation is supported by the recent observation that bioaccumulation potential increases ten fold for every additional  $CF_2$  unit within the alkyl chain for perfluoroacids (Martin *et al.*).

## Fate Pathways

### 10) Atmospheric Degradation Processes (Ellis & Martin)

The telomer alcohols are proposed to degrade in the atmosphere following a mechanism outlined in Figure 8.

#### 6:2 FTOH Tropospheric Reactions; Possibilities

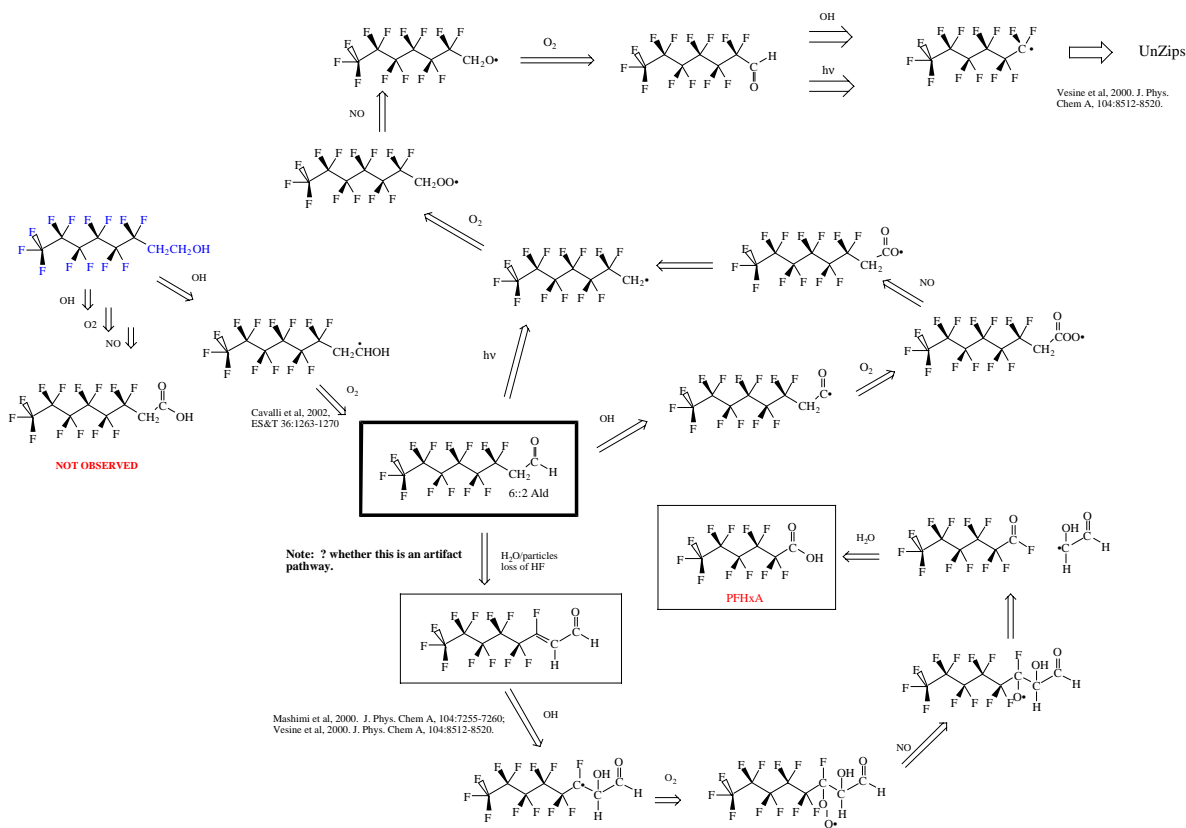


Figure 8. Proposed atmospheric degradation of Telomer alcohols, 6:2 alcohol is used as an illustrative example.

This hypothesis was tested using a 10m<sup>3</sup> artificial atmospheric smog chamber. The 6:2 alcohol was introduced to the system along with cyclohexane (a reference compound), NO gas, and isopropyl nitrite (an indirect source of OH). The system was irradiated using black lights and sample aliquots were taken and analyzed as a function of time. Real time NO<sub>x</sub> and O<sub>3</sub> concentrations were monitored in order to eliminate possible secondary loss reactions. Samples were collected in real time by SPME and analyzed using GC/MS. Samples were also taken using XAD and Na<sub>2</sub>CO<sub>3</sub> denuders, low temperature gas phase condensation bubblers, and by passing gas samples through DNPH SPE cartridges for further analysis. Continuous air flow from the chamber was passed through nylon and XAD coated filters which were collected and analyzed for particulate formation. Post chamber analyses were conducted using <sup>19</sup>F NMR, LC/MS/MS and GC/MS.

The telomer alcohol does not undergo photolysis at the wavelengths of light used and it does not undergo significant wall reactions, or with NO<sub>x</sub> and O<sub>3</sub> under the conditions used. The gas phase condensate obtained from the smog chamber at low temperature (-78°C) by bubbling the air through acetone was analyzed directly using <sup>19</sup>F NMR. The resultant spectra, acquired over a 24-hour period clearly indicated the presence of the 6:2 alcohol and a second fluorinated species that we have tentatively assigned as fluoride. No other fluorinated intermediates were observed, possibly due to the low concentrations of fluorinated intermediates coupled with the low sensitivity of the NMR experiment. GC/MS analysis of samples acquired by passing smog chamber air through an XAD bed have thus far only indicated the presence of starting material. Due to the volatility of the proposed intermediates it was recognized this may be result of poor trapping efficiency. Larger volumes of air have been passed icwe pre-coated XAD denuders that have a greater capacity for such materials. These samples are currently being analyzed.

The pseudo first order kinetics for the reaction of the 6:2 telomer with OH relative to cyclohexane is shown in Figure 9.

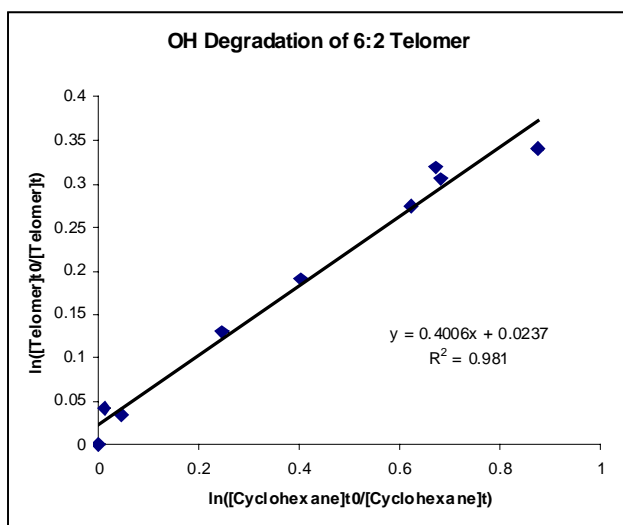


Figure 9. Relative rates of reaction for cyclohexane with 6:2 telomer

Using a rate constant of  $7.49 \times 10^{-12}$  molecule  $\text{cm}^3 \text{s}^{-1}$  at 298K for the reaction of OH with cyclohexane resulted in a calculated rate constant for the 6:2 telomer alcohol of  $2.8 \pm 0.1$  molecule  $\text{cm}^3 \text{s}^{-1}$  ( $n=2$ ). The reported literature value for the OH initiated degradation of butanol is  $8.24 \pm 0.84 \times 10^{-12}$  molecule  $\text{cm}^3 \text{s}^{-1}$  which is as expected greater than the measured value for the 6:2 telomer alcohol due to the effect of fluorination. However, this rate is greater than would be predicted using the Kwok and Atkinson method of prediction. We believe that this is a result of secondary, through space interaction of the ethanolic substituent with the fluorinated tail of the molecule, a hypothesis that is supported by MS data obtained (details of which are presented in above) and from the literature dealing with similar compounds. The product perfluorohexanoic acid was positively identified ( $n=3$ ) by LC/MS/MS (Figure 10) and is currently being quantified relative to the starting material ~ it does not appear to be the major route for degradation. Overall we have had significant difficulties in isolating and identifying the bulk of the FTOH degradation products. For instance we've only obtained sporadic evidence for the initial aldehyde via GC/MS and we do observe fluoride in some samples. These results may indeed indicate that the 'unzipping' route is the dominate fate pathway for the FTOHs (see Fig 8). A good deal of further work must be done obtaining a mass balance of products and confirming the degradation pathway.

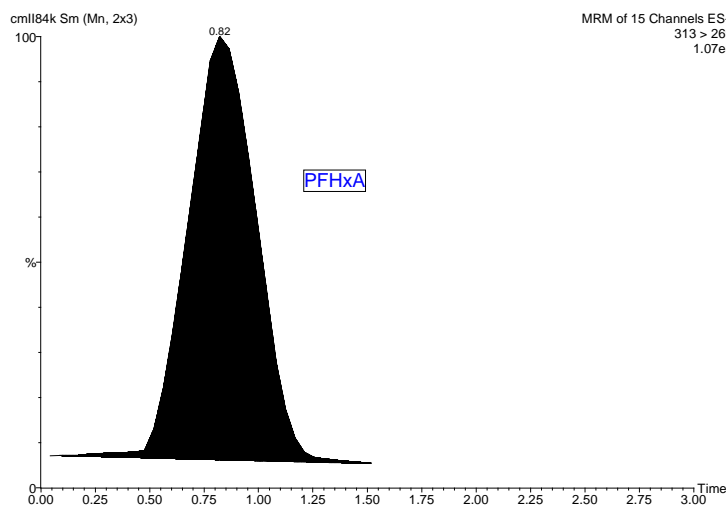


Figure 10. LC/MS/MS indicating the production of perfluorohexanoic Acid

The proposed intermediate aldehyde and acids (Section 5) that potentially lead to the formation of perfluorohexanoic and longer chain acids (Figure 5) were synthesized by the methods outlined in Figure 8 for the use as standards for the identification of these intermediates.

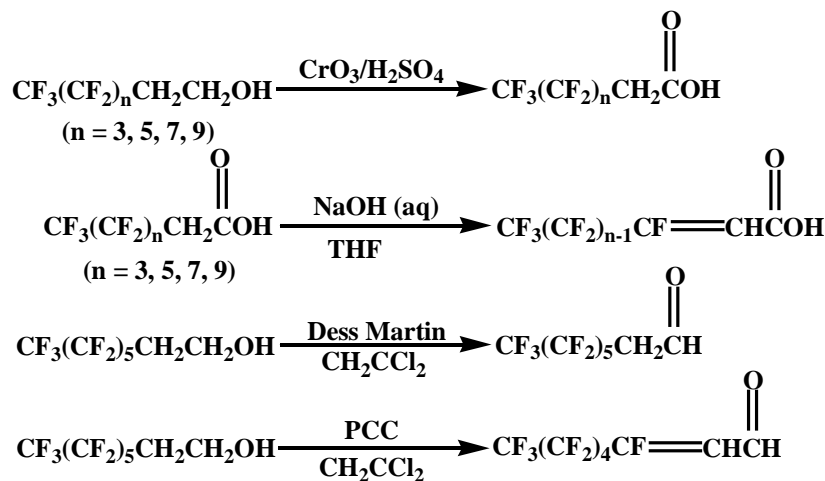


Figure 11. Synthesis of fluoro aldehyde and acid standards.

A further interesting observation is that 1H,1H,2H,2H perfluorodecylidide, which is an impurity contained within the manufactured 6:2 telomer, is not observed to degrade under these conditions, thus indicating greatly reduced reactivity with OH and ultimately a much longer tropospheric lifetime.

### 11) Biodegradation of FTOHs (Ye & Dinglasan)

Range finding experiments have been initiated on the suite of FTOHs with initial experiments focused on the fate of the 6:2 FTOH in a mixed culture of microbes. Mixed enrichment aerobic degrading cultures were obtained from a 1, 2 DCA site in LA, U.S. and subsequently maintained on either 1,2 DCA or ethanol. Two isolates have been identified to date from this mixed culture ~ a *Ralstonia sp.* and a *Xanthobacter sp.*. These experiments have clearly shown that the 6:2 fluorotelomer alcohol is efficiently oxidized to the 6:2 telomer acid (see Fig 12) which then either hydrolyzes or further metabolizes to the 6:2  $\alpha,\beta$  acid. Low but clearly measurable quantities of the perfluoroacid PFHxA are observed to build up in the reaction vessels. Work currently is focused on optimizing analytical methods to monitor all compounds of interest during the biodegradation experiment with particular focus on observing the relevant intermediates (e.g. the 6:2 aldehyde which has been synthesized). To accurately determine the reaction pathway subsequent experiments will dose the microbial media with the 6:2 aldehyde, acid, alpha-beta acid, and PFHxA in order to obtain rates and pathway information on each. We will then compare the relative susceptibilities of the 4:2 through 10:2 FTOHs and confirm whether the degradation pathway is similar across the varied chain length.



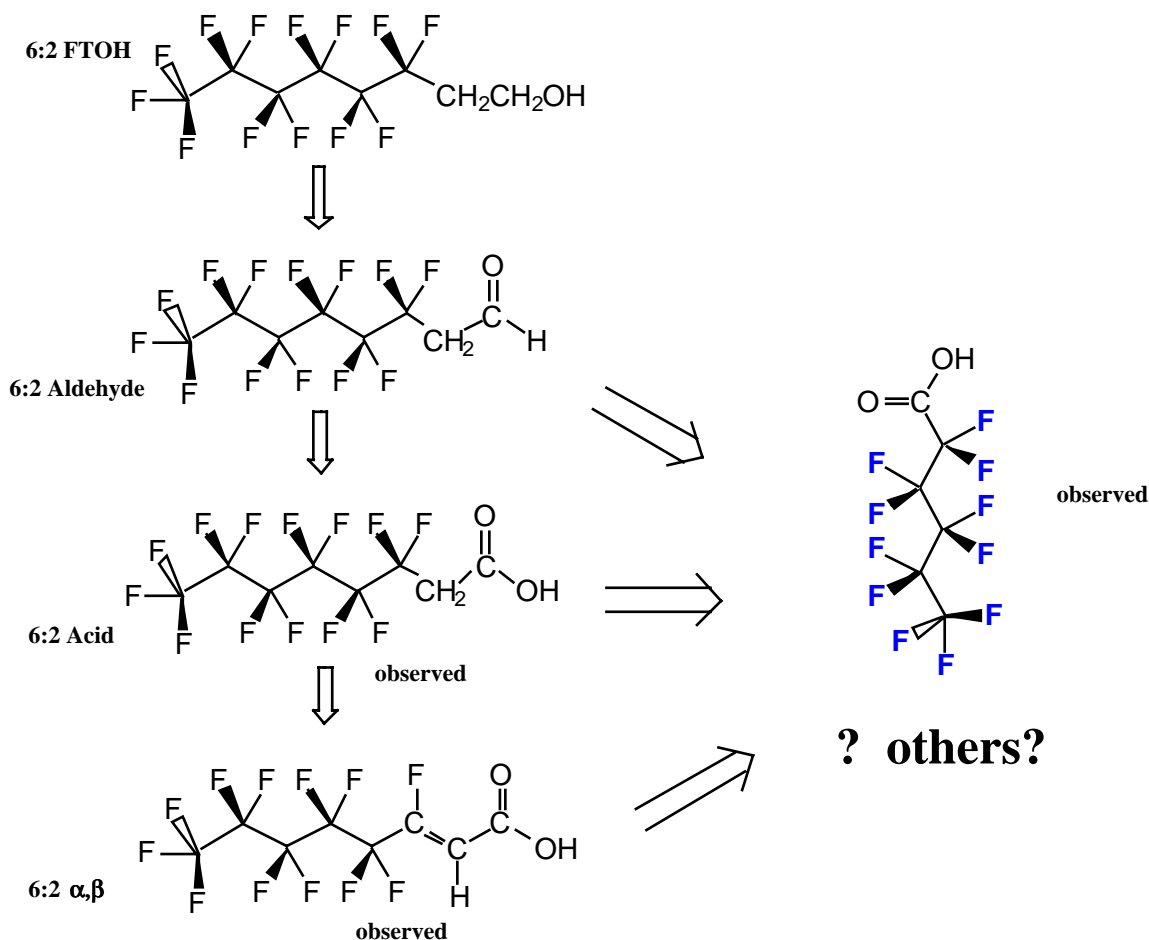


Figure 12. Proposed biodegradation pathway of 6:2 FTOH with intermediates so far confirmed by LC/MS/MS. We are unclear specifically where PFHxA arises but it appears to follow the build up slowly after high concentrations of the 6:2  $\alpha,\beta$  acid are formed.

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## Presentations

- S.A. Mabury, "Environmental and Analytical Chemistry of Fluorinated Surfactants". DIOXIN 2002, Barcelona, Espana, August, 2002. Invited Speaker, Organizer of the session on "New POPs". Published Short Paper in "Xenobiotics".
- S.A. Mabury, "Fluorinated Chemicals in the Environment ~ Redefining Persistence?" GLRM.American Chemical Society, Minneapolis, MN, June, 2002. Invited platform.
- Martin, J.W., Muir, D.C.G., Stock, N., Moody, C.A., Ellis, D.A., Kwan, W.C., Mabury, S.A. "Detection of Fluorinated Organic Contaminants in Atmospheric Samples by GC/CI/MS". International Association of Great Lakes Research 45th Annual Conference, Winnipeg, May, 2002. Platform Presentation.
- S.A. Mabury, "Redefining Persistence ~ Fluorinated Chemicals in the Environment". Environalysis 2002. Toronto, ON. May, 2002. Invited Keynote.
- S.A. Mabury, "Flights of Fancy ~ Fluorinated Chemicals in the Environment". University of California-Davis. May, 2002. Invited Seminar.
- S.A. Mabury, "Perfluorinated Surfactants in Environmental Samples ~ Analysis by LC/MS/MS." 223<sup>rd</sup> American Chemical Society, Environmental Chemistry Division. April, 2002. Invited Platform.
- S.A. Mabury, "19F NMR in Analytical Chemistry", Asia-Pacific Conference on Analytical Science, 19-22 Feb, 2002, Shangri-La Hotel, Manila, Philippines. Invited Keynote Speaker.

S.A. Mabury, "Analytical and Environmental Chemistry of Fluorinated Pollutants", Department of Chemistry, University of the Philippines-Los Banos, Feb, 2002. Invited Seminar.

S.A. Mabury, "Carbonate Radical and the PhotoFate Test System. Institute of Chemistry, University of the Philippines-Diliman, Feb, 2002. Invited Seminar.

S.A. Mabury, "A New Class of Pollutant ~ Fluorinated Compounds", Natural Science Research Institute, University of the Philippines-Diliman, Feb, 2002. Invited Seminar.

S.A. Mabury, "Fluorinated Chemicals in the Environment: Analytical and Environmental Chemistry" Stanford University, Nov. 30, 2001. Invited Seminar.

S.A. Mabury. "What Makes a Chemical a Pollutant". Inaugural speaker in the "University of Toronto Lecture Series in Markham". October 3, 2001. Invited platform.